European research platform IPANEMA at the SOLEIL synchrotron for ancient and historical materials

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IPANEMA, a research platform devoted to ancient and historical materials (archaeology, cultural heritage, palaeontology and past environments), is currently being set up at the synchrotron facility SOLEIL (Saint-Aubin, France; SOLEIL opened to users in January 2008). The new platform is open to French, European and international users. The activities of the platform are centred on two main fields: increased support to synchrotron projects on ancient materials and methodological research. The IPANEMA team currently occupies temporary premises at SOLEIL, but the platform comprises construction of a new building that will comply with conservation and environmental standards and of a hard X-ray imaging beamline today in its conceptual design phase, named PUMA. Since 2008, the team has supported synchrotron works at SOLEIL and at European synchrotron facilities on a range of topics including pigment degradation in paintings, composition of musical instrument varnishes, and provenancing of medieval archaeological ferrous artefacts. Once the platform is fully operational, user support will primarily take place within medium-term research projects for 'hosted' scientists, PhDs and post-docs. IPANEMA methodological research is focused on advanced two-dimensional/three-dimensional imaging and spectroscopy and statistical image analysis, both optimized for ancient materials.

Keywords: archaeological materials; palaeontology; conservation science; art history; X-ray imaging; X-ray spectroscopy; data analysis.

1. Introduction: current trends in the synchrotron study of ancient and historical materials

We group here, under the generic term 'historical and ancient materials', materials of archaeological, palaeontological, palaeo-environmental and cultural heritage interest. Despite their great diversity, these materials share common features in the context of their synchrotron-based study: (*a*) they are often highly heterogeneous and/or composite at successive length scales; (*b*) their properties out of equilibrium are of major interest; (*c*) they often take their full historical meaning once considered within corpuses and collections of objects; (*d*) some artefacts may require adapted handling and/or storage conditions. These features guide the entire characterization methodology from sample preparation to data processing.

The use of synchrotron-radiation-based techniques for various categories of ancient materials has already been reviewed by a number of authors (Harbottle *et al.*, 1986; Mommsen *et al.*, 1996; Janssens *et al.*, 2000, 2010; Pantos *et al.*, 2004; Salvadó *et al.*, 2005; Creagh, 2006; Tafforeau *et al.*, 2006; Bertrand, 2007; Sutton, 2008; Cotte *et al.*, 2009a,b, 2010; Bertrand *et al.*, 2011b). In recent years many spectacular synchrotron experiments have been performed in the field of ancient and historical materials, resulting in more than 600 publications between 1986 and 2011, with a strong increase over the past ten years (Fig. 1). Major synchrotron techniques employed are hard X-ray microfocused and imaging techniques [X-ray diffraction (XRD), X-ray fluorescence (XRF), X-ray absorption spectroscopy (XAS), computed tomography (CT); Fig. 2(*a*)]. However, over the past five years, evolutions
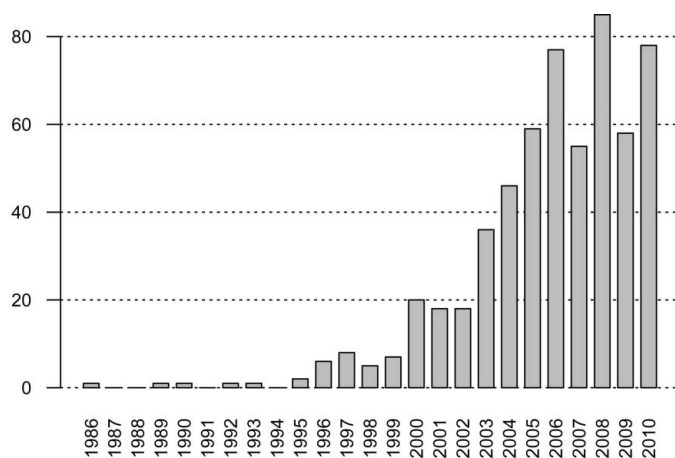
Figure 1
Evolution of the number of publications per year using synchrotron radiation for ancient and historical materials known to the authors in the time frame 1986–2010 (N = 583). Recent evolution may partly be connected to the closure of LURE (Orsay, France) and SRS (Daresbury, UK), two facilities that accounted in total for more than 20% of the published synchrotron literature in the fields of ancient and historical materials.

have been observed regarding the state-of-the-art synchrotron analysis of ancient and historical materials (Fig. 2*b*). The main orientations are briefly outlined hereafter.
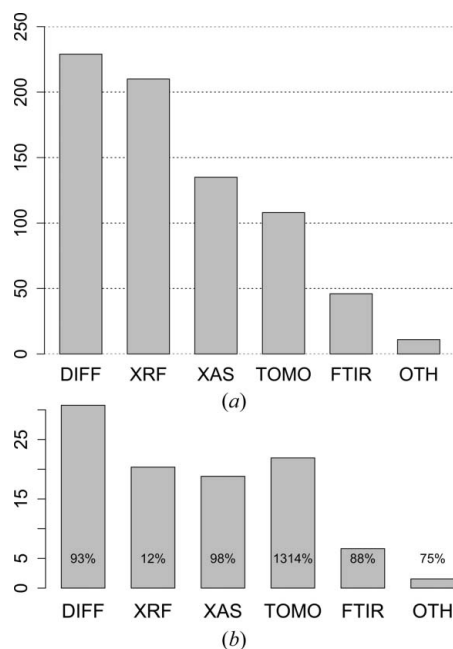

Figure 2
Distribution in the main categories of techniques used in the synchrotron study of ancient materials, based on the number of publications known to the authors. DIFF: X-ray diffraction and scattering; XRF: X-ray fluorescence; XAS: X-ray absorption spectroscopy; TOMO: X-ray tomography and laminography; FTIR: Fourier-transform infrared microspectroscopy; OTH: STXM, X-PEEM and XPS, UV–visible spectroscopy. (*a*) Total number of publications in the 1986–2010 period. (*b*) Share (in %) of each category in the 2005–2010 period. Figures on the bars represent the increase in use of the techniques from the 2001–2005 to the 2006–2010 period. Note the very strong increase in tomographic techniques, although today mainly restricted to palaeontological studies.

XRD is an essential tool for phase identification of ancient materials. Knowledge of the phases inside the sample allows identification of materials in the sample, for example pigments in paint layers (de Nolf & Janssens, 2010), and can help in the understanding of the manufacturing process (see, for example, Liu *et al.*, 2007). The use of high-energy (>50 keV) XRD is becoming more common as it allows the surface layers of absorbing samples like bronze to be penetrated (Young *et al.*, 2010). A method not so commonly used for ancient and historical materials is small-angle X-ray scattering (SAXS). However, as many samples contain particles or structures of 1–100 nm length scale (Colomban, 2009; Fermo *et al.*, 2002; Hiller & Wess, 2006; Padeletti & Fermo, 2003; Reibold *et al.*, 2006), it might become more prominent in the future.

XRF is a major method for the semi-quantitative and quantitative determination of elemental composition, employed mainly in conjunction with other synchrotron measurements that can be carried out at the same point of analysis such as XRD and XAS. Two trends are observed: (i) interest for confocal hard-X-ray XRF to attain depth sensitivity in fluorescence elemental measurements in the study of sub-surface stratified systems or inclusions of typical dimensions in the few tens of to few micrometres ranges (Woll *et al.*, 2008; Mantouvalou *et al.*, 2008), although the difficulty of solving the inverse problem still hampers the method of obtaining high-resolution three-dimensional reconstruction of complex and heterogeneous systems, and (ii) the development of fast elemental X-ray imaging methods of flat heritage artefacts, such as easel paintings, drawings and fossils using both synchrotron *K*-edge imaging (Krug *et al.*, 2006) and fast XRF raster macro-scanning (Dik *et al.*, 2008; Bergmann *et al.*, 2010).

X-ray absorption spectroscopy is a method so far specific to synchrotron sources that can lead to the determination of the speciation of almost any element, based on the study of the fine variations of the absorbance when scanning the absorption edge of an element. The method proved particularly efficient in studying the complex speciation encountered within altered materials such as paints (Robinet *et al.*, 2011*b*; Monico *et al.*, 2011) or archaeological artefacts (Monnier *et al.*, 2010). Over the recent period, X-ray absorption has been used at softer energies, typically a few keV, to study *K*-edges from light elements and *L*-/*M*-edges from transition and heavy metals.

The use of synchrotron X-ray micro-computed tomography techniques for ancient materials has taken off in the past five years. μCT allows three-dimensional reconstructions based on local variations of the material density, and more generally that of their complex refractive index, both in a non-invasive and non-destructive manner. The very small source size attained at third-generation synchrotron sources and novel coherence-based imaging approaches are optimal for 'edge enhancement' by simple propagation of the beam passing through the scanned object, phase reconstruction and holographic approaches, resulting in greatly facilitated segmentation of the data (Tafforeau *et al.*, 2006). Palaeontological specimens were imaged at high spatial resolutions, including

studying preserved soft tissues, incremental features of dental materials and specimens included in fossil amber (Pradel *et al.*, 2009; Tafforeau & Smith, 2008; Smith *et al.*, 2009; Soriano *et al.*, 2010; Kruta *et al.*, 2011).

Fourier-transform infrared micro-spectroscopy (FT-IR) remains an essential technique for the identification and mapping/imaging of mostly organic as well as inorganic or hybrid materials within multilayer or heterogeneous matrices. The complementary use of synchrotron FT-IR and infrared imager microscopes is of great interest in cultural heritage studies for obtaining, respectively, high signal-to-noise spectra of materials with an image of their spatial distribution over large areas (Cotte *et al.*, 2005; Bertrand *et al.*, 2011*a*). The attenuated total reflection (ATR) FT-IR technique, often used to overcome the difficulties in analysing samples in reflection and to access higher spatial resolution, has spread in laboratories over the last five years and is just emerging at synchrotrons (Spring *et al.*, 2008; Mazzeo *et al.*, 2007; Sloggett *et al.*, 2010).

A limited group of additional techniques have occasionally been used in ancient materials studies in the X-ray (STXM, XPS and X-PEEM) and UV–visible ranges. Soft/tender X-ray methods such as scanning transmission X-ray microscopy (STXM) and X-ray photoelectron emission microscopy (X-PEEM) provide images of the chemical speciation of light elements such as carbon, nitrogen or oxygen. This opens the way to the identification of ancient organic biomolecules at a spatial resolution of a few tens of nanometres, for instance in heavily diagenetized fossils (Bernard *et al.*, 2007, 2009; Benzerara *et al.*, 2008). Methods providing speciation from the photoelectrons generated during photoexcitation, such as X-ray photoelectron spectroscopy (XPS) and X-PEEM, require ultra-high-vacuum set-ups, whereas STXM can be performed in helium atmosphere. Another important difference is the need to cross-section samples in STXM, while X-PEEM is performed on a clean sample surface (Boyce *et al.*, 2010). Measures to mitigate radiation damage are essential, particularly for soft X-rays as the materials' cross sections are much greater than at higher energies. Novel UV–visible spectroscopy and imaging techniques were developed in the context of IPANEMA and are presented in §3.2.

All these techniques are available worldwide on most synchrotron sources, except UV–visible techniques. In particular, at SOLEIL, hard X-ray microtomography techniques will be implemented at the PSICHE and PUMA beamlines, in absorption and phase-contrast mode, respectively. Hard X-ray micro-focused techniques will also be installed at PUMA. X-PEEM and STXM will be available at the HERMES beamline. All the other techniques mentioned are already available.

2. Overview of the IPANEMA platform

2.1. Main objectives of IPANEMA

The field addressed by the European research platform for ancient materials, IPANEMA (in French, 'Institut Photonique d'Analyse Non-Destructive Européen des Matériaux Anciens'; 'European Institute for the Photon-Based Non-Destructive Analysis of Ancient Materials'), includes four application fields: archaeology, cultural heritage, palaeontology and palaeo-environments, based on two areas of methodological research: photon-based imaging/spectroscopy, and data processing/analysis of ancient and historical materials.

The Heritage and Archaeology Liaison Office (HALO) was created at Synchrotron SOLEIL following a synchrotron radiation workshop and the joint initiative from CNRS (Groupement de Recherche 'SOLEIL and Heritage') and SOLEIL to foster the implementation of a dedicated infrastructure at SOLEIL for these fields of research (Bertrand *et al.*, 2006). The bases of IPANEMA were further refined during the meeting of four thematic working groups (archaeometry/archaeology, conservation science/art history, palaeontology, palaeo-environments) within three dedicated meetings in 2008 and two workshops "IPANEMA'09, A beamline for ancient materials at SOLEIL" and "IPANEMA'11, Synchrotron radiation for ancient materials", respectively, held at the facility in May 2009 and January 2011. SOLEIL is a third-generation synchrotron light source located 25 km southwest of Paris. It consists of a linac and booster synchrotron and a storage ring of circumference 354 m. The synchrotron operates at a storage-ring energy of 2.75 GeV and uses a beam current of 400 mA (500 mA in commissioning) in top-up mode. The very small vertical emittance allows high-brilliance experiments. In total, SOLEIL will contain 29 beamlines (including PUMA, set up in the framework of IPANEMA), of which 17 are open to users as of March 2011. The set of beamlines cover an extensive energy range from the far infrared to hard X-rays, giving rise to ample opportunities for cultural heritage experiments.

The implementation of IPANEMA relies on four main components: a dedicated team, a new building at the SOLEIL site, a new beamline PUMA optimized for ancient materials, and adapted procedures such as access modalities for corpuses and collections of objects at SOLEIL. At the date of the publication of this article, the team is installed in temporary premises at the SOLEIL site, with a temporary preparation room that today includes tools for mechanical sample preparation, infrared and electron microscopy equipments. The new building of the platform is in construction and PUMA is in its conceptual review design phase. From 2007 to 2008, IPANEMA started developing research on ancient and historical materials through its two main modalities: (*a*) support to synchrotron projects, (*b*) dedicated methodological research activities. The present article aims at presenting the new infrastructure, discussing the main scientific targets of the project and describing the first works undertaken at IPANEMA.

2.2. Support to ancient materials synchrotron projects

IPANEMA aims at supporting access to all synchrotron beamlines at SOLEIL and future partner synchrotron facil-

research papers

ities. Additional actions are developed to support projects from non-expert users.

For the first three years of operation of SOLEIL, a total number of 109 ancient materials projects[1] were submitted to SOLEIL, among which 61 were accepted (oversubscription: 1.8). These proposals were submitted to the normal peer-review system of SOLEIL, with a varying level of implication from IPANEMA from no support at all to full participation to the experiment preparation, execution and data processing. At the opening of the platform building, scheduled in 2013, increased support will be brought to experiments of 'hosted scientists' (up to 20 PhD students, post-docs, researcher *etc.*) on medium-term projects, as well as regular short synchrotron proposals. Hosted scientists will act as temporary contact points for external groups and be trained on the instrument in the practical use of synchrotron methods. Hosted projects supported by IPANEMA will focus on corpuses (series, collections) of samples or collections of artefacts in order to meet with the needs expressed by the disciplines. This includes redundant studies of key statistical series of historical artefacts and samples, in addition to the more conventional case studies performed at large-scale facilities.

The European Commission set up a trans-national access scheme to IPANEMA/SOLEIL through the CHARISMA (Cultural Heritage Advanced Research Infrastructures: Synergy for a Multidisciplinary Approach to Conservation/Restoration) integrating activity project (CHARISMA, 2009). SOLEIL is a member of the French platform of CHARISMA with the ion beam accelerator AGLAE (Centre de recherche et de restauration des musées de France, C2RMF, Paris), while a Hungarian platform groups installations from the Laboratory of Ion Beam Applications (Institute of Nuclear Research, Hungarian Academy of Sciences, Debrecen) and the Budapest Neutron Centre (Institute of Solid State Physics and Optics, Hungarian Academy of Sciences, Budapest).

From 2004, IPANEMA has been organizing 'New Lights on Ancient Materials' (2004, 2007, 2010), a European training cycle targeted at the use of synchrotron techniques to study ancient and historical materials.

2.3. Development of the PUMA beamline

The large oversubscription of third-generation synchrotron beamlines strongly hampers the investigation of statistically relevant sets of samples. In addition, specific conservation, security and safety requirements cannot always be satisfied at conventional beamlines. For this reason, the PUMA (in French, 'Photons utilisés pour les matériaux anciens') beamline is being constructed at SOLEIL that will be optimized for the needs of ancient and historical materials, but open to all fields of research. The PUMA beamline will consist of two endstations, one for microfocus techniques and the other for full-field imaging. The source for PUMA will be a wiggler (see parameters in Table 1) which is currently under study at SOLEIL. To achieve sufficient phase contrast the experi-

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[1] We distinguish here proposals submitted to several beamlines into distinct 'projects'.

Table 1
Summary of the recommended specifications for (*a*) the micro-focused imaging and (*b*) the full-field imaging endstations of the PUMA beamline.

These values are based on suggestions and recommendations from the user community that have been collected in conferences and workshops, such as the IPANEMA'11 workshop that was held in January 2011 at SOLEIL.

Parameter	Target value
Beamline name	PUMA
Source	Wiggler, 164 mm × 20 periods, B = 1.8 T
Mirror	Ir-coated, fixed angle, bendable
(*a*) Micro-focused imaging	
Methods	µXRF, µXAS, µXRD
Monochromator	Si 111
Spectral range	4–22 keV; optimal 8–18 keV
Spectral resolution	$\sim 10^{-4}$
Spot size (unfocused)	>100 µm × 100 µm FWHM
Spot size (focused)	3 µm × 3 µm FWHM
(*b*) Full-field imaging	
Methods	Absorption, phase-contrast µCT
Monochromator	Ir (12 Å)/B$_4$C (12 Å) multilayer
Spectral range	20–60 keV (optimum 40–60 keV)
Spectral resolution	$\sim 10^{-2}$
Field of view	>20 mm × 10 mm (H × V) FWHM
Coherent lengths	40 µm × 40 µm FWHM

mental hutch will be located in an external building, 75 m away from the source. When performing microspectroscopy experiments, a horizontal mirror is used for harmonic rejection and prefocusing, while the same mirror is used for the creation of a virtual source in full-field mode (see below). The beamline is currently in the early design phase and is expected to accommodate its first users in late 2015. In the following we describe the design goals of PUMA; however, a full technical description will be published once the beamline is constructed.

Microfocus experiments use X-ray optics to focus the beam on the sample. The most important microfocus techniques for the PUMA beamline are XAS, XRF and XRD. As the energy of the incoming beam has to be scanned for XAS, a Kirkpatrick–Baez mirror system will be used for achromatic focusing. The degree of focusing should be optimized for the common samples investigated in cultural heritage and ancient materials research. While these materials are extremely varied and show many successive spatial heterogeneity length scales, a submicrometre beam is only required for a limited number of studies which can be satisfied by specialized beamlines. The target beam size for PUMA is 3 µm × 3 µm, which offers sufficient resolution for most materials at stake, while not sacrificing too much flux, and preserving a rather uncluttered sample environment. In addition, it will be possible to use the endstation with an unfocused beam of 0.1–1 mm diameter for experiments that do not need a high degree of spatial resolution. A system for quick and robust change between focused and unfocused mode will be implemented.

To satisfy the energy resolution needed for absorption spectroscopy and diffraction experiments, a double-crystal Si 111 monochromator (DCM) will be used. The mirror is used for harmonics rejection, which is especially important for XAS measurements. The energy range covered should include all

the major edges relevant for research on ancient materials that can be accessible without vacuum environment (Cotte *et al.*, 2010). It will include the *K*-edges of important transition metals such as Mn (6.5 keV), Fe (7.1 keV) and Cu (9.0 keV) and special efforts will be made to reach the Ca *K*-edge at 4.0 keV. This endstation will be designed for operation up to 22 keV.

Full-field-imaging techniques measure the radiation transmitted by the sample. In most cases the absorption contrast of the sample is used. However, for objects such as palaeontological specimens of rather homogeneous composition, the absorption contrast is very weak. In this case a great enhancement of the image quality can be achieved by techniques that make use of the phase contrast of the sample. The prerequisite for this is a small source size and a long distance between the source and the sample, corresponding to a transverse coherence length of 40 µm × 40 µm. The small vertical emittance at SOLEIL is sufficient for phase-contrast experiments; however, in the horizontal direction a secondary source is needed, which will be created by focusing the beam with the horizontal mirror on a pair of slits ∼5 m downstream.

Imaging experiments do not need a high energy resolution. Multilayer monochromators provide monochromatic beams with a large bandwidth (typically 10^{-2}) and can deliver a flux typically two orders of magnitude higher than a DCM. The energy range of this endstation needs to be sufficiently high to penetrate large samples, as they are frequently found in palaeontological investigations. For this reason, an energy range between 20 and 60 keV is targeted, which will offer enough penetration power to image palaeontological specimens, archaeological and conservation materials of up to a few centimetres thickness. A summary of the specifications requested for the PUMA beamline can be found in Table 1.

2.4. Methodological research at IPANEMA

The IPANEMA methodological research activity is initially structured along two main axes: multiscale and multimodal imaging and spectroscopy of ancient materials; and information retrieval, analysis and modelling for ancient materials.

On the imaging and spectroscopy side, the development and implementation of X-ray imaging approaches for ancient and historical materials will intensify in the context of the definition and implementation of the new PUMA beamline. IPANEMA aims at facilitating the coupling of complementary synchrotron approaches and laboratory methods, initiated on the infrared and X-ray sides. Methods of synchrotron-radiation-based spectroscopy and imaging that are currently underdeveloped for ancient materials but appear promising will be studied, starting by new methods in UV–visible imaging and spectroscopy (see below). The high intensity of focused third-generation synchrotron beams makes considerations of radiation damage important, especially for soft-matter samples. IPANEMA will therefore take part in the developments to reduce and monitor sample degradation in the beam.

Regarding statistical image analysis, initial efforts from IPANEMA will focus both on the reconstruction, approximation of spectral imaging of ancient material and classification, image segmentation adapted to the complexity of studied samples and corpuses (see below). The nature of the encountered materials, composite, heterogeneous and often non-reproducible, will be the driving force to develop an original activity at the cross-roads between signal processing and statistical modelling.

In the longer term, the local expertise in instrumentation will enable the development of new adaptive processes and new sensing modalities, combining control, acquisition and data processing.

3. First highlights

3.1. First supported synchrotron projects

The first works listed below were supported at SOLEIL by IPANEMA, in the context of regular synchrotron proposals. Various levels of support were brought to the projects from contribution to sample preparation, data collection or data processing to a more integrated approach where the whole methodological approach was jointly determined with the external user group and the involved beamline scientists. These projects were carried out at several beamlines of SOLEIL: CRISTAL, DIFFABS, DISCO, LUCIA, SMIS and TEMPO, and at the FLUO beamline of ANKA, before the opening of the future PUMA beamline. The absence of microtomography beamlines for the time being at SOLEIL constrains the use of the facility for palaeo-environmental sciences and palaeontology, resulting primarily in first tests in the field. So far, main works on ancient materials have therefore been performed in archaeology and conservation sciences.

The finishing techniques of historical musical instruments from the 16th to the 18th century were studied with the Cité de la Musique using synchrotron FT-IR at the SMIS beamline (Dumas *et al.*, 2006) and UV–visible spectromicroscopy and imaging at DISCO (Jamme *et al.*, 2010). The high signal-to-noise spectra collected at the synchrotron source were used to better identify and map the major organic and inorganic compounds contained in the distinct varnish strata (Echard *et al.*, 2008, 2010; Bertrand *et al.*, 2011*a*). In particular, varnishes from five musical instruments by A. Stradivari were shown to be based on a simple oil-based recipe.

The discolouration of smalt, a blue pigment widely used by artists in paintings between the 16th and 18th century, has been investigated in collaboration with the National Gallery London and the C2RMF (Paris). The combination of synchrotron micro X-ray absorption spectroscopy (XANES and EXAFS) at the Co *K*-edge on the LUCIA beamline and infrared microspectroscopy on the SMIS beamline was applied to smalt-containing paints samples. The microfocused measurements revealed the local and medium-range structural modifications associated with the alteration, in particular the

coordination change of cobalt responsible for the colour alteration of the pigment (Robinet *et al.*, 2011*a,b*).

Prussian blue (PB) is an iron-based pigment that was widely used in Europe in the 18th and 19th centuries. Exposed to light or to anoxic treatments, Prussian-blue-containing artifacts sometimes discolour owing to a photoreduction of iron III into iron II. The purpose of this study, led by the Smithsonian Institution, is to determine the role of the substrate in the fading process. Structural and chemical changes associated with the discolouration of model PB artifacts (*i.e.* Prussian blue dyed on textiles, laid on papers and embedded in gelatin) were studied by synchrotron X-ray diffraction (CRISTAL beamline) and X-ray absorption spectroscopy (DIFFABS beamline). First results confirmed a reduced Fe-III:Fe-II ratio in faded samples confirming the photoreduction process. However, a more complex structural modification seems to take place, exemplified by the high variation of the XANES region with the type of substrate (*e.g.* paper *versus* gelatin) or the oxidation capacity of the substrate (*e.g.* neutral cellulosic *versus* light-sensitive lignin-containing paper). Comparison between PB powder and PB laid on paper without light treatment also stressed out the capacity of a substrate to modify the structure of the pigment, even without the catalytic effect of light (Gervais *et al.*, 2011).

The long-term degradation of bones from archaeological settings was studied by synchrotron FT-IR at the SMIS beamline, complementing laboratory-based spectroscopy and imaging with the C2RMF and the Department of Prehistory, National Museum of Natural History, Paris. Results of their long-term degradation features in sediments highlight the spatial variability at the microscale of the bone composition and structure after long-term ageing (Lebon *et al.*, 2011).

The trace-elemental content of slag inclusions in ferrous artefacts was shown to contribute to provenance studies of medieval metal artefacts. Confocal XRF measurements were performed at the FLUO microprobe at ANKA (Simon *et al.*, 2003). The composition of inclusions of a few tens of micrometres in diameter were used to complement stylistic data on finely worked Milanese and Brecian armours in good agreement with micro-destructive LA-ICP-MS measurements (Leroy *et al.*, 2011). Furthermore, new multivariate statistical tests were developed to better provenance artefacts based on the trace-elemental content of slag inclusions.

'Colorando Auro' is a project developed by A. Crabbé and H. Wouters at KIK-IRPA (Bruxelles, Belgium), that aims to study the techniques of the colouring of gold applied on silver plates, for which recipes are described in medieval manuscripts (Crabbé *et al.*, 2008). Photoemission experiments have been performed on the TEMPO beamline (Polack *et al.*, 2010) on model samples in order to determine the reaction mechanism and to characterize the surface species that could be responsible for the colouration.

3.2. Progress in methodological developments

On the methodological side, a first area is the development and adaptation of novel synchrotron UV–visible methods.
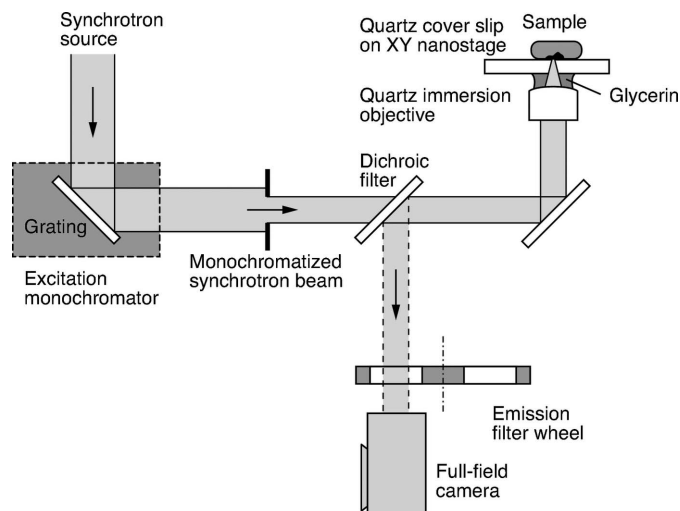

Figure 3
Adaptation of the full-field micro-imaging endstation of the DISCO beamline at SOLEIL (M. Réfrégiers, Fr. Jamme) by addition of a filter wheel in front of the detection camera. This set-up allowed the full-field imaging of luminescence signals of areas of 151 µm × 202 µm with a projected pixel size of 290 nm on historical and reference cross sections. Samples were deposited on a quartz cover slip mounted on the *XY* nanostage of an inverted microscope (Thoury *et al.*, 2011).

Two modalities, raster-scanning microspectrometry and full-field micro-imaging for historical samples, were implemented and tested at the DISCO beamline (Giuliani *et al.*, 2009; Jamme *et al.*, 2010) of SOLEIL (Fig. 3). The use of the synchrotron UV–visible source and of custom-made quartz optics at DISCO leads to an extended wavelength range down to the VUV (180 nm) with a high spatial resolution (typically 300 nm), a very high level of monochromaticity and continuous tunability over the whole 180–600 nm range, able to selectively analyse compounds bearing luminophores in historical and archaeological cross sections. The interest of this novel approach was tested on zinc white (ZnO)-based paints and organic binders in historical cross sections (Thoury *et al.*, 2011). Synchrotron UV–visible luminescence could be used in the future to study a large variety of samples that present characteristic luminescence signals in the UV and visible domain, be they organic (such as dyes, resins and proteinaceous materials), inorganic (semiconductor based pigments) or mixed. Specific labelling agents could also be used on some materials. Working at such a high spatial resolution allows both better understanding the material in relation to complementary spatially resolved characterization, and facilitating the disentanglement of the complex luminescence signal collected when studying mixtures of compounds. The method is complementary to measurements performed at a lower spatial resolution using conventional sources.

On the data-processing side, preliminary results of information retrieval were obtained by extending Gaussian mixture modelling to segment spectromicroscopy images (Cohen & Le Pennec, 2011). The method uses stochastic modelling of the spectra by a Gaussian mixture thus leading to a natural classification of the pixels of the image. Still, the method is original in that it takes into account, as part of the
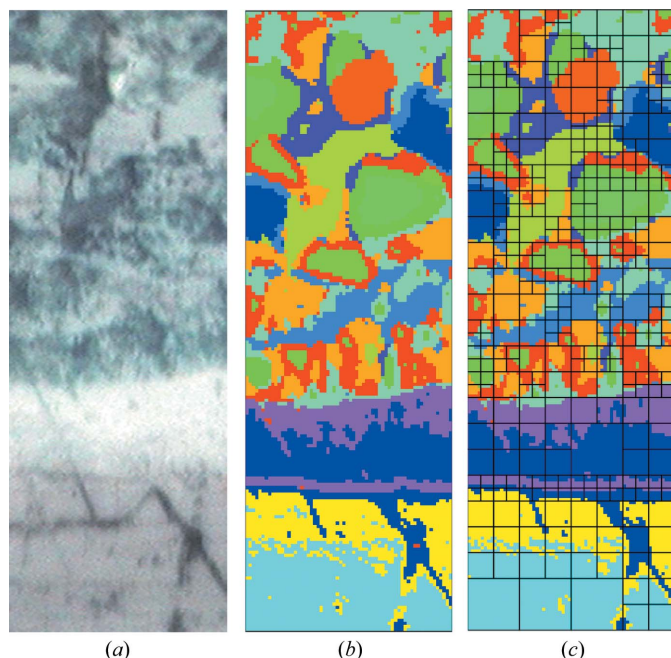
Figure 4
(a) Light microscopy area of a mock-up paint sample stratigraphy (sample UD1, 2000, National Gallery London) mapped by Ge ATR-FTIR (4000–700 cm^{-1}) coupled to a linear array detector (64 × 192 pixels with 1.56 µm spacing). From bottom to top, embedding resin (polyester), ground layer (lead white in oil), painted layer (azurite and lead white in oil). (b) Classification result on spectra not taking into account their pixel position. Each colour corresponds to one of the 15 classes used in the classification. (c) Result obtained by the spatially enhanced Gaussian mixture modelling. The squares denote zones of identical stochastic distribution of spectra.

design of the data acquisition, the spatial nature of the data points. In other words the statistical model used is such that it spatially regularizes the classification to favour 'large' uniform patches. Fig. 4 shows a comparison between clustering performed using regular Gaussian mixture modelling (b) and spatially enhanced Gaussian mixture stochastic modelling of spectra (c). One can see that most of the outliers (single pixel of a class surrounded by one or few other classes) have been regularized, as well as the borders of the patches.

4. Discussion and conclusions

This paper reflects the current state of development of the European ancient materials IPANEMA platform, today in construction at the site of the SOLEIL synchrotron (Saint-Aubin, France). The main orientations were defined from contributions of thematic working groups, and the practical implementation of the platform concepts will certainly benefit from additional contributions. The first works were supported in the field. The opening of the platform building and the arrival of the first 'hosted scientists', scheduled in two years time, will certainly be a major step in the setting up of the platform. IPANEMA research activities on instrumental development and data analysis are gradually being developed.

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